dimethyl ester hydrochloride, 68781-29-3; DL-*threo*-3-fluoroaspartic acid dimethyl ester hydrochloride, 68781-30-6; L-threonine, 72-19-5; L-allothreonine, 28954-12-3; D-threonine, 632-20-2; D-allothreonine, 24830-94-2; DL-*threo*-3-hydroxyaspartic acid dimethyl ester hydrochloride, 13515-98-5.

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Thermolysis of 1-*n*-Butoxy-1-(*tert*-butylperoxy)ethane[1]

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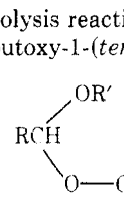
The monoperoxy acetal 1-*n*-butoxy-1-(*tert*-butylperoxy)ethane (1), prepared by the acid-catalyzed addition of *tert*-butyl hydroperoxide to *n*-butyl vinyl ether, undergoes pyrolysis at temperatures above 120 °C. The major pyrolysis products of 1 are methane, *tert*-butyl alcohol, *n*-butyl formate, and *n*-butyl acetate. The formate/acetate ratio depends on the reaction temperature, the concentration of the peroxy acetal, and the solvent in which the thermolysis is performed. Decomposition of 1 in *tert*-butylbenzene, a solvent in which the acetate/formate ratio is greater than unity, is faster than in cumene, a solvent in which the acetate/formate ratio is less than unity. The effects of solvent on the thermolysis rates and the product distributions are explained in terms of two modes of decomposition of 1, a unimolecular homolysis of the peroxide function that yields the formate ester and a free-radical chain reaction that accounts for the formation of the acetate ester.

Monoperoxy acetals have been prepared by the addition of an alkyl hydroperoxide to a vinyl ether,[1] by the transacetalation of acetals with an alkyl hydroperoxide,[2] by displacement reactions of alkyl hydroperoxides on α-halo ethers,[3] by alkylation of either peroxy hemiacetals or α-hydroperoxy ethers,[4] and by Cu_2Cl_2-catalyzed oxidation of ethers with an alkyl hydroperoxide. The predominant reaction products of the pyrolysis of these compounds have been reported to be the alcohol R″OH, the carboxylate ester RCO_2R', the formate ester HCO_2R', and the hydrocarbons derived from the alkyl moiety R.[6] The present work describes the kinetics and products of the thermolysis reactions in *tert*-butylbenzene and in cumene of 1-*n*-butoxy-1-(*tert*-butylperoxy)ethane (1),



1, $R = CH_3$; $R' = n\text{-}C_4H_9$; $R'' = t\text{-}C_4H_9$

the addition product of *tert*-butyl hydroperoxide and *n*-butyl vinyl ether. *tert*-Butylbenzene and cumene were chosen as solvents for these reactions because they differ in their capabilities of reacting with chain-carrying peroxide-derived radicals, the latter having a benzylic hydrogen reactive toward abstraction by free radicals, whereas the *tert*-butylbenzene, having only primary alkyl hydrogens, is less reactive toward reaction with peroxide-derived radicals.

Results

Gas chromatographic examination of the reaction products obtained in the thermolysis of 1 in both cumene and *tert*-butylbenzene showed that the only nongaseous compounds formed in measurable amounts are *tert*-butyl alcohol, *n*-butyl acetate, and *n*-butyl formate. Methane, identified gas chromatographically, was the only gaseous product observed. Gas chromatographic analyses of the reaction mixtures of the decomposition of 1 in cumene and in *tert*-butylbenzene at different temperatures and solvent/peroxide ratios are shown in Table I. The reliability of these data is evident from the agreement between the amount of 1 that has reacted and the amount of *tert*-butyl alcohol and the sum of the amounts of the esters formed. Examination of the kinetic data and the product distributions shows the following facts that require explanation in terms of the mechanism for the thermolysis of this monoperoxy acetal. (1) The decomposition rate is faster at a given concentration ratio and temperature in *tert*-butylbenzene than in cumene. (2) The acetate/formate ratio is greater than unity in *tert*-butylbenzene but less than unity in cumene. (3) The acetate/formate ratio is dependent on the concentration of the peroxy acetal, the effect being more pronounced in *tert*-butylbenzene than in cumene.

Discussion

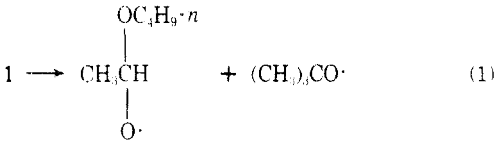
A mechanism for the thermal decomposition of 1 in a solvent RH capable of hydrogen abstraction by peroxide-derived radicals consistent with the observed experimental data is shown in eq 1–6. The amount of *n*-butyl formate formed in the fragmentation of 2 serves as a measure of the amount of 1 that decomposes in the unimolecular homolysis. If radical 2 participated in a hydrogen atom abstraction, the hemiacetal $CH_3CH(OH)OC_4H_9\text{-}n$ would have been formed. Since no detectable amounts of either acetaldehyde or *n*-butyl alcohol were observed, it is reasonable to conclude that the formation

Table I. Thermolysis Reactions of 1

time, min	1, mmol	acetate/formate	products, mmol		
			t-BuOH	HCO_2Bu-*n*	CH_3CO_2Bu-*n*
tert-butylbenzene (5:1 mole ratio)[a] at 120 °C ($t_{1/2}$ = ~160 min)					
0	20.48				
50	15.85	1.69	5.34	1.78	3.02
100	12.11	1.67	8.91	3.20	5.34
150	10.50	1.59	10.15	3.92	6.23
200	9.08	1.58	11.93	4.27	6.76
250	8.19	1.54	12.82	4.63	7.12
300	5.76	1.43	13.89	5.16	7.48
350	5.87	1.39	14.96	5.87	8.19
tert-butylbenzene (10:1 mole ratio)[b] at 120 °C ($t_{1/2}$ = ~220 min)					
0	11.34				
50	8.55	1.38	2.80	1.24	1.71
100	7.46	1.36	4.04	1.71	2.33
150	6.53	1.35	5.13	2.18	2.95
225	5.59	1.29	6.05	2.64	3.42
375	3.88	1.33	7.61	3.26	4.35
450	3.42	1.31	7.92	3.57	4.66
tert-butylbenzene (5:1 mole ratio)[c] at 135 °C ($t_{1/2}$ = ~28 min)					
0	10.65				
15	7.25	1.47	3.58	1.48	2.18
38	4.71	1.31	5.85	2.53	3.31
48	3.93	1.30	6.72	2.96	3.84
59	3.32	1.28	7.07	3.14	4.01
cumene (5:1 mole ratio)[d] at 120 °C ($t_{1/2}$ = ~280 min)					
0	20.57				
50	17.07	0.64	3.19	1.75	1.12
100	15.63	0.68	5.42	3.03	2.07
150	13.71	0.72	7.34	3.99	2.87
200	12.28	0.72	9.25	5.10	3.66
250	12.21	0.70	10.68	5.90	4.15
300	9.25	0.74	11.96	6.70	4.95
350	8.13	0.71	12.76	7.18	5.10
cumene (10:1 mole ratio)[e] at 120 °C ($t_{1/2}$ = ~312 min)					
0	10.39				
50	8.84	0.44	1.82	1.26	0.56
100	7.22	0.50	2.66	1.68	0.84
150	6.73	0.63	3.65	2.25	1.41
225	5.89	0.68	4.63	2.67	1.82
300	5.47	0.58	5.47	3.37	1.97
375	4.63	0.63	6.32	3.79	2.39
450	3.65	0.65	7.30	4.35	2.81
cumene (5:1 mole ratio)[f] at 135 °C ($t_{1/2}$ = ~40 min)					
0	10.18				
15	8.02	0.61	2.56	1.44	0.88
38	5.29	0.69	5.13	2.89	2.01
48	4.11	0.60	5.77	3.61	2.17
59	3.69	0.63	6.66	4.09	2.57

[a] 3.82 g of 1 in 13.99 g of *tert*-butylbenzene. [b] 2.08 g of 1 in 13.46 g of *tert*-butylbenzene. [c] 2.06 g of 1 in 6.67 g of *tert*-butylbenzene. [d] 3.93 g of 1 in 12.02 g of cumene. [e] 1.95 g of 1 in 12.08 g of cumene. [f] 1.91 g of 1 in 6.11 g of cumene.

of *n*-butyl formate via the fragmentation reaction 3 is a measure of the amount of 1 that undergoes unimolecular homolysis, yielding radical **2** along with the *tert*-butoxyl radical. The amount of *n*-butyl acetate, on the other hand, is a measure of the amount of 1 that decomposes in the chain sequence 5 and 6. The extent to which chain sequence 5 and 6 is operative depends on the partitioning of the chain-carrying *tert*-butoxyl radical between reaction with 1 (eq 5) and the solvent (eq 2). It is significant that the acetate/formate ratios observed



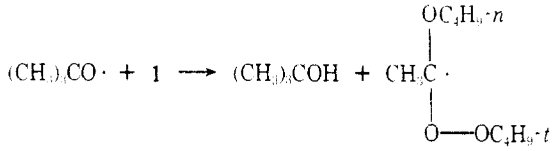
$$1 \longrightarrow CH_3\underset{\underset{O\cdot}{|}}{\overset{\overset{OC_4H_9\text{-}n}{|}}{C}}H + (CH_3)_3CO\cdot \qquad (1)$$

2

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \qquad (2)$$

$$\mathbf{2} \longrightarrow CH_3\cdot + HCO_2C_4H_9\text{-}n \qquad (3)$$

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \qquad (4)$$



$$(CH_3)_3CO\cdot + 1 \longrightarrow (CH_3)_3COH + CH_3\underset{\underset{O-OC_4H_9\text{-}t}{|}}{\overset{\overset{OC_4H_9\text{-}n}{|}}{C}}\cdot \qquad (5)$$

3

$$\mathbf{3} \longrightarrow (CH_3)_3CO\cdot + CH_3CO_2C_4H_9\text{-}n \qquad (6)$$

for the decompositions in *tert*-butylbenzene, a solvent that is less reactive toward hydrogen abstraction than cumene, are greater than unity, indicating that more than half of 1 decomposed by the chain mechanism in *tert*-butylbenzene. The acetate/formate ratio for the decompositions in cumene, on the other hand, is less than unity, indicating that less than half of 1 decomposed in the chain sequence, presumably because the chain-carrying *tert*-butoxyl radicals are effectively intercepted by the cumene.

The extent to which the peroxy acetal 1 decomposes in the chain sequence is also dependent on the concentration of 1 as evidenced by the fact that the acetate/formate ratio is greater in the more concentrated solutions of 1. The effect is less pronounced in the reactions performed in cumene than those in *tert*-butylbenzene, the solvent in which more of the peroxy acetal decomposes in the chain reaction, and therefore more susceptible to factors that influence the amount of 1 that participates in the chain sequence. The decrease in the acetate/formate ratios observed for the reactions in *tert*-butylbenzene as the reaction proceeds merely reflects the expected concentration effect; namely, at lower concentrations of the peroxy acetal 1, less of 1 participates in the chain sequence 5 and 6. The analytical techniques employed apparently are not sensitive enough to detect similar concentration effects which may be operative to a lesser extent in the decompositions performed in cumene.

The more rapid rates of decomposition of 1 in *tert*-butylbenzene relative to the decomposition rates in cumene also reflect the greater extent to which 1 reacts via the chain sequence in *tert*-butylbenzene than in cumene. The rate law for the decomposition of 1 is the sum of the rates of the reactions in which 1 reacts, namely, reactions 1 and 5 (eq 7). The contribution of the second term of the rate law 7 to the observed rate law depends, of course, on the amount of 1 that decomposes in the chain sequence. The kinetic order of 1 in the observed rate law depends on both the contribution of the second term of eq 7 to the overall decomposition rate and the rate-limiting step in the chain sequence 5 and 6. If the kinetic chain length of the chain sequence is long, the most probable termination would be the cross termination reaction 8, and the rate law for the reaction would be first order in 1 (eq 9). Inspection of the half-lives of 1 (see Table I) at 120 °C at two concentrations indicates that in both solvents the reaction is not first order since the decomposition rate is faster for the more concentrated solutions of 1. It is significant also that the effect of increasing the concentration of 1 by a factor of 2 on its decomposition rate is more pronounced (37.5% increase) in *tert*-butylbenzene, the solvent in which the decomposition of 1 via the chain sequence is the more important reaction path, than in cumene (11.4% increase), the solvent in which the unimolecular decomposition path predominates.

$$-\mathrm{d}[1]/\mathrm{d}t = k_1[1] + k_5[(\mathrm{CH_3})_3\mathrm{CO}\cdot][1] \qquad (7)$$

$$3 + (\mathrm{CH_3})_3\mathrm{CO}\cdot \xrightarrow{k_8} \text{termination product} \qquad (8)$$

$$-\mathrm{d}[1]/\mathrm{d}t = (k_1 + k_1k_5k_6/k_8)[1] \qquad (9)$$

A kinetic order for 1 that is greater than unity is consistent with the derived rate law 10. This rate law requires that reaction 5 be the rate-limiting step in the chain sequence and that termination of the chain occurs only by the reaction of the chain-carrying radicals involved in the rate-limiting step of the chain sequence, namely, the coupling of *tert*-butoxyl radicals (eq 11).

$$-\mathrm{d}[1]/\mathrm{d}t = k_1[1] + (k_1/2k_{11})^{1/2}k_5[1]^{3/2} \qquad (10)$$

$$2(\mathrm{CH_3})_3\mathrm{CO}\cdot \xrightarrow{k_{11}} (\mathrm{CH_3})_3\mathrm{COOC}(\mathrm{CH_3})_3 \qquad (11)$$

If the fragmentation reaction 6 were the rate-limiting step of the chain sequence, termination would occur via a bimolecular reaction of the chain-carrying radicals 3 (eq 12), and the derived rate law for the reaction (eq 13) indicates that the observed rate law would require a kinetic order for 1 that is less than unity if any appreciable amounts of 1 decompose in the chain reaction.

$$2\ \mathbf{3} \xrightarrow{k_{12}} \text{termination products} \qquad (12)$$

$$-\mathrm{d}[1]\mathrm{d}t = k_1[1] + (k_1/2k_{12})^{1/2}k_6[1]^{1/2} \qquad (13)$$

Finding that only the derived rate law 10 is consistent with the observed kinetic data, namely, that the kinetic order of 1 is greater than unity, suggests that hydrogen abstraction of the α-hydrogen from the peroxy acetal 1 is the rate-limiting step of the chain sequence. The unimolecular fragmentation of the peroxy acetal derived radical 3 by reaction 6, therefore, is a facile process. A similar conclusion was reached concerning the fragmentation of the 2-(*tert*-butylperoxy)propyl radical 4 encountered in the decomposition of isopropyl *tert*-butyl peroxide.[8]

$$\underset{\mathbf{4}}{(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OOC}(\mathrm{CH_3})_3} \rightarrow (\mathrm{CH_3})_2\mathrm{C{=}O} + \cdot\mathrm{OC}(\mathrm{CH_3})_3 \qquad (14)$$

Experimental Section

1-*n*-Butyl-1-(*tert*-butylperoxy)ethane (1). *n*-Butyl vinyl ether (0.40 mol, Aldrich) was added dropwise to a stirred solution consisting of a small amount of *p*-toluenesulfonic acid in 96% *tert*-butyl hydroperoxide (0.3 mol). The temperature of the reaction mixture was maintained at 10 °C during the addition. After stirring for about 5 h at ~10 °C, the reaction mixture was diluted with 50 mL of ether and the solution was extracted three times with 10% NaOH solution and dried over anhydrous magnesium sulfate. After removal of the ether, the 1-*n*-butyl-1-(*tert*-butylperoxy)ethane (68% of theory) was distilled (bp 48 °C at 2 mm, $n^{20}{}_{\mathrm{D}}$ 1.4068).

Decomposition Studies. Reaction mixtures consisting of 1 and either *tert*-butylbenzene (Aldrich) or cumene (Matheson) in the molar ratios shown in Table I were prepared and sealed in 9 mm Pyrex tubes which were placed in an oil bath set at the appropriate temperature. Tubes were removed at the designated times shown in Table I and cooled, and the weighed portions of the reaction mixtures were mixed with a weighed amount of ethyl benzoate, which served as an internal standard for the gas chromatographic analysis of the unreacted peroxide and the reaction products. The gas chromatographic separations were accomplished on an 8 ft × 0.25 in. column packed with DC-200 on Chromasorb W.

Reaction mixtures consisting of a 5:1 molar ratio of the solvents when heated to 120 °C in a flask attached to a mercury-filled gas buret evolved a gaseous product which was identified as methane by comparison of its gas chromatographic retention time on a Poropak Q column with that of an authentic sample of methane. No other gaseous products were observed.

Registry No.—1, 68367-48-6; *n*-butyl vinyl ether, 111-34-2; *tert*-butyl hydroperoxide, 75-91-2; *tert*-butyl alcohol, 75-65-0; *n*-butyl formate, 592-84-7; *n*-butyl acetate, 123-86-4; methane, 74-82-8.

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